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6. AUTHOR(S) Dr. Ekaterina Kalabukhova							
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Institute of Semiconductor Physics Lysogorskaya str. 4, Kiev 252028 Ukraine			8. PERFORMING ORGANIZATION REPORT NUMBER N/A				
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**ІНСТИТУТ ФІЗИКИ
НАПІВПРОВІДНИКІВ**

252028, Київ-28, пр.Науки, 45
ФАКС 38 (044) 228 72 72
Ел.пошта: mickle@semicond.Kiev.ua

National Academy of Sciences
of Ukraine

**INSTITUTE OF
SEMICONDUCTOR PHYSICS**

45, Pr. Nauki, Kiev, 252028, Ukraine,
FAX 38(044) 228-72-72
E-mail: mickle%semicond.Kiev.ua@ts.Kiev ua

Dr. C. Martin Stickley,
Chief, Lasers, Optics and Materials
Air Force EOARD
223/231 Old Marylebone Road, London,
UK NW1 5TH

Dr. E.N.Kalabukhova
Head of the Wide Band Gap
Semiconductor Material
Sciences Department
June, 5, 1998.

Dear Dr. C. Martin Stickley,

In accordance with the Research Program of "Investigations of the Temperature and Concentration Dependencies of ESR Spectrum of Residual Donors in 6H SiC" (Project SPC-98-4055), accepted in Wright Air Force Lab. by Dr. W.C.Mitchel and Dr. E.N.Kalabukhova I am sending you the final Report of our research results "ESR Spectra of Residual Donors Inherent n-type bulk 6H SiC".

Sincerely



E.N.Kalabukhova.

Final Report**ESR Spectra of Residual Donors Inherent n-type bulk 6H SiC .****(Project SPC - 98 - 4055)**

There is some dispute in the literature whether nitrogen is only residual shallow donor or whether there is a second level due to a structural defect. Carlos at all [1] resolved in 3C SiC of n-type two donor spectra in the temperature interval of 10-40 K: one triplet lines associated with nitrogen and a broader line of unidentified origin coincided with the central line of nitrogen triplet lines at 9 GHz. Veinger [2] investigated the behavior of donor ESR spectra in 6H SiC with uncompensated donor concentration ($N_D - N_A$) from $1 \cdot 10^{17}$ to $6 \cdot 10^{18} \text{ cm}^{-3}$ in the temperature interval from 77 K to 125 K. He observed one triplet lines associated with nitrogen in two cubic sites I_{k1}, I_{k2} and broader line coincided with the central line of nitrogen triplet lines at 9GHz. The additional line was interpreted as exchange line appeared in nitrogen ESR spectrum due to non - localized electrons in the concentration range of $1 \cdot 10^{17}$ to $6 \cdot 10^{18} \text{ cm}^{-3}$. Such interpretation of donor ESR spectra in 6H SiC has been generally accepted up to now.

But the drawback of the works mentioned above is that the investigations were carried out in the narrow temperature interval and the effect of the variation of the magnetization of ESR signals with the temperature were not accounted by using the calibrated sample with the ESR signal obeyed the Curie law that has led to the mistakes in interpretation ESR results and in obtaining energetically characteristics from ESR data.

In this work we report the results of ESR investigations of 6H SiC Lely grown samples with uncompensated donor concentration ($N_D - N_A$) from $3 \cdot 10^{18}$ to $1 \cdot 10^{16} \text{ cm}^{-3}$ in the temperature interval from 4.2 K to 160 K obtained at 9 and 140 GHz to establish the number of donor centers inherent n-type bulk 6H SiC samples.

Fig.1, 2 shows ESR spectrum of 6H SiC in wide temperature interval at 9 GHz and 140 GHz. At high temperature for the samples with donor

concentration from $2 \cdot 10^{18}$ to $1 \cdot 10^{16} \text{ cm}^{-3}$ ESR spectrum consist of one single line I_D while at low temperature one consist of two triplet lines I_{k1} , I_{k2} associated with the nitrogen in two cubic sites coincided with each other at 9 GHz and single line I_h associated with the nitrogen in hexagonal position which coincided with resonance field of the central triplet line at 9 GHz. When the concentration increase up to $3 \cdot 10^{18} \text{ cm}^{-3}$ at high temperature the ESR spectrum is also consist of broad single line but at low temperature an additional wide exchange S-line appeared against the background of the nitrogen ESR spectrum (see Fig. 1b, 2b). As was shown in [3], the exchange S-line consists of two S_1 and S_2 lines and at low temperature originates from variable-range hopping motion donor electron between one of the cubic (K_1 , K_2) occupied and hexagonal unoccupied site. With increasing the temperature up to 35 K the width of S_1 and S_2 -lines decrease while the g-value of those changes and approaches the center gravity of ESR spectrum of nitrogen at cubic sites I_{k1} and I_{k2} , respectively, due to combined effect of hopping motion and direct Heisenberg exchange between paramagnetic centers.

The temperature range of detection of donor ESR spectra depend from the donor concentration. With decreasing of donor concentration from $3 \cdot 10^{18}$ to $1 \cdot 10^{16} \text{ cm}^{-3}$ the temperature at which the intensities of donor ESR lines decrease are shifted to the higher temperature.

It should be noted that at low temperature for the samples with donor concentration less than $8 \cdot 10^{17} \text{ cm}^{-3}$ the intensity of nitrogen ESR lines decrease and saturation effects become noticeable for nitrogen ESR spectrum, especially at 140 GHz. (It is known that the power, for example of 5 mW, at 140 GHz generates the same microwave strength as 500 mW in X-Band).

With increasing the microwave power the nitrogen ESR spectrum is saturated and eventually one single line I_D remains in ESR spectrum indicating the different spin-relaxation time of two paramagnetic centers, see Fig. 3. This suggests that the single line I_D , which has a shorter spin-relaxation time, is a second donor center.

Fig. 4 shows the temperature dependencies of the relative integral intensities of donor ESR spectra for the samples with uncompensated donor concentration ($N_D - N_A$) in the range of $3 \cdot 10^{18}$ to $8 \cdot 10^{17} \text{ cm}^{-3}$ which are described by

$$N_D = \frac{I_D(T)}{I_{\text{ref}}(T)} \cdot \frac{1}{T} \cdot (\Delta H_D)^2 \approx \exp\left(-\frac{E_D}{kT}\right) \quad (1),$$

where N_D - concentration of paramagnetic donor centers, $I_D(T)$, $I_{\text{ref}}(T)$ - are the intensities of donor and reference ions lines. ΔH_D - is the width of between points of maximum slope of absorption line.

The intensity of single I_D ESR line one can obtain as the difference between the intensity of the central and one side triplet line. Due to the ESR line of nitrogen in hexagonal site decreased in intensity and disappeared about of 45-60 K for the samples of different degree of compensation ($N_D - N_A$) the central line is not influenced that at the temperature higher than 60 K. At the same time the intensity of ESR line of nitrogen at hexagonal site one can also obtain as the difference between the intensity of the central and one side triplet lines. The ESR line I_D is not influenced the central line at low temperature due to the ESR spectrum was recorded at low level of microwave power to avoid the saturation of nitrogen ESR spectrum.

The relative integral intensities were estimated by comparison with the line intensity of reference sample of MgO with low concentration of Cr^{3+} ions obeyed the Curie law. The resonance line of reference sample has $g=1.9799$ closed to that of nitrogen in SiC. The sample and reference sample are mounted simultaneously at one position in the cavity. When the width of the line changes as a function of temperature, the effect of amplitude of magnetic field modulation was accounted.

At high temperature the intensities of donor ESR lines decrease is apparently due to ionization of donors. The number of ionized donor electrons is proportional to the number of electrons excited to the conduction band which is at low temperature given by

$$n_o \approx \beta N_c \left[\frac{N_D - N_A}{N_A} \right] \exp\left(-\frac{E_D}{kT}\right) \quad (2),$$

where N_c and β are the conduction band density of states and degeneracy, respectively, N_D and N_A are the donor and acceptor concentrations and E_D - energy ionization of donor.

As follows from (2) the number of excited electrons depends from the degree of compensation. Indeed, the same number of excited electrons could be obtained with the different ratio of N_D/N_A at the different temperature. When the degree of compensation is rather large and N_D/N_A approaches unit the temperature of ionization in exponential must be higher to give the same number of excited electrons. As was seen from Fig. 4 similar behavior has been observed in the temperature dependencies of intensities of donor ESR lines when ($N_D - N_A$) changes from $3 \cdot 10^{18} \text{ cm}^{-3}$ to $1 \cdot 10^{16} \text{ cm}^{-3}$. With increasing the degree of compensation the temperature at which the intensity of ESR lines begin to decrease are shifted to the higher temperature. The same is valid for the donor line widths which are broadening at higher temperature for the samples with high compensation due to exchange interaction between donor and conduction electrons [4].

Fig. 5 shows the temperature dependence of central triplet line width for donor concentration of $1 \cdot 10^{16} \text{ cm}^{-3}$ - $2 \cdot 10^{18} \text{ cm}^{-3}$. In the concentration range of $1 \cdot 10^{16} \text{ cm}^{-3}$ - $2 \cdot 10^{18} \text{ cm}^{-3}$ the line width has appreciably weaker temperature dependence compared with that for the sample with donor concentration of $3 \cdot 10^{18} \text{ cm}^{-3}$. This indicates that above the donor concentration of $2 \cdot 10^{18} \text{ cm}^{-3}$ the central triplet line contains a second unresolved component due to I_S - exchange line which is narrowed in the temperature interval from 4.2 K to 40 K (see Fig. 6) and than begin strongly broadening at high temperature caused by the change of the character of the electrons from localized state to the non - localized state. More detailed experimental studies would be clarify the phenomena of high-temperature behavior of I_S -line.

The curves $\ln(N_D(T))$ versus the inverse temperature are plotted by experimental points in Fig. 7. From the slope of the curves one can obtain the energy characteristics of donor centers. At the donor concentration higher than $1 \cdot 10^{18} \text{ cm}^{-3}$ the values of energy $E_i = 150 \text{ meV}$ and 80 meV obtained for nitrogen in cubic and hexagonal sites respectively are consisted with the value of energy ionization of nitrogen in 6HSiC. When the concentration decrease high temperature slope of nitrogen ESR line at cubic sites give the energy ionization of about 63 meV which is consisted with the value of valley-orbit splitting for nitrogen at two cubic sites known from Raman measurements [5].

Conclusion.

1. The 6H SiC sample with donor concentration in the range from $2 \cdot 10^{18} \text{ cm}^{-3}$ to $1 \cdot 10^{16} \text{ cm}^{-3}$ in the temperature interval of 4.2 K to 140 K revealed two donor ESR spectra: one associated with the nitrogen in inequivalent positions (I_{k_1}, I_{k_2}, I_h) and single line (I_D), while at donor concentration higher than $2 \cdot 10^{18} \text{ cm}^{-3}$ additional exchange I_S -line appeared in donor ESR spectrum and originates from hopping motion electrons between localized state at low temperature and non-localized electrons at high temperature.

The single I_D -line should be attributed to second residual donor inherent 6H SiC n-type Lely grown samples. Having been observed at higher temperature than nitrogen, the second residual donor is considered to be deeper than nitrogen.

2. The deviation from Curie law of the temperature dependencies of intensities of the donor ESR lines were discovered. The peaks observed in the temperature dependencies are direct evidence for electron redistribution between the multiple donor levels when the temperature changes.
3. Correlation between the temperature of ionization of paramagnetic donor centers and degree of compensation of the samples was established.
4. The values of ionization energy $E_i = 150 \text{ meV}$ and 80 meV of nitrogen in cubic and hexagonal sites, respectively were determined for the samples with

donor concentration higher than 10^{18}cm^{-3} , while in the range of low concentration when the concentration of non - localized electrons is low the high temperature slope of integral intensities of ESR line give the value of energy ionization of about 63 meV which is consisted with the value of valley-orbit splitting for nitrogen at two cubic sites.

Literature.

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ESR Spectrum of Residual Donors Inherent n-type 6H SiC grown by sublimation - sandwich method.

Now we focus on 6H SiC samples grown by sublimation sandwich method (SSM) at $T = 1800$ C with growth velocity varying from 0.5 mm/h to 1mm/h and donor concentration in the range of $2 \cdot 10^{16} \text{ cm}^{-3}$ - $3 \cdot 10^{17} \text{ cm}^{-3}$.

The ESR study has two principle objectives:

1. To verify the validity of results obtained for 6H SiC lely grown sample to 6H SiC grown by SSM.
2. To compare the characteristics of 6HSiC samples using dissimilar techniques: ESR, Hall, DLTS, TAS.

Temperature behavior of ESR spectrum was studied on two series samples.

One series comprised 6H SiC grown at $T = 1800$ C with a growth velocity of $V_g = 0.5 \text{ mm/h}$ and donor concentration of $(2 - 4) \cdot 10^{16} \text{ cm}^{-3}$ (I90); $(6 - 8) \cdot 10^{16} \text{ cm}^{-3}$ (I91.1). In a second series 6H SiC grown at $T = 1850$ C with growth velocity of $V_g = 1.0 \text{ mm/h}$ and donor concentration of $(7 - 9) \cdot 10^{16} \text{ cm}^{-3}$ (R31), $3 \cdot 10^{17} \text{ cm}^{-3}$ (1020.AM).

The difference between two sample series becomes evident even in comparison the ESR spectrum of those at high temperature. In first series of samples ESR spectrum consist of one single I_D -line while second series of samples exhibit only two triplet lines I_{k1} , I_{k2} from nitrogen on cubic sites coincided with each other at 9 GHz, (see Fig. 8, 10). The low temperature ESR spectra measured at 140 GHz of both sample series showed the known spectra of nitrogen (labelled I_{k1} , I_{k2} , I_h in Fig. 9, 11) and a new spectrum (labelled I_{nd2} in Fig.11) appeared only in the second sample series grown at high velocity.

The complete angular dependence of donor ESR spectra of second series of sample shows that the new ESR spectrum consist of one single line (see Fig. 12) with axial symmetry about the c-axis with $g_{||} = 2.00447$, $g_{\perp} = 2.0026$.

Comparison the temperature dependencies of relative integral intensities of donor ESR spectra of 6H SiC Lely grown samples and grown by SSM, shown in Fig. 13, 14, indicated that the first series of sample has the similar behavior

of ESR spectra as those for 6HSiC Lely grown samples with the same donor concentration and revealed two donor ESR spectra: one associated with nitrogen and second due to deeper than nitrogen donor of unknown nature. This in contrast to what is observed for the second sample series having a substantial different temperature dependence compare to Lely grown sample (see fig.15). The most striking difference between two series of samples comes from the temperature behavior of second residual donors I_D and I_{nd2} appeared in ESR spectrum of nitrogen. ESR spectrum of I_{nd2} donor and nitrogen on cubic site are observed in the same temperature interval whereas ESR spectrum of I_D is ionized at the temperature higher than nitrogen ESR spectrum. This indicates that the I_D residual donor is consistent with deeper than nitrogen energy level whereas I_{nd2} donor should be attributed to shallower donor than nitrogen with energy level located between nitrogen energy levels. This conclusion is consisted with the value of energy ionization $E_D \approx 100 - 120$ meV obtained from high temperature slope of temperature dependence of intensity of I_{nd2} -ESR line, shown in Fig. 16.

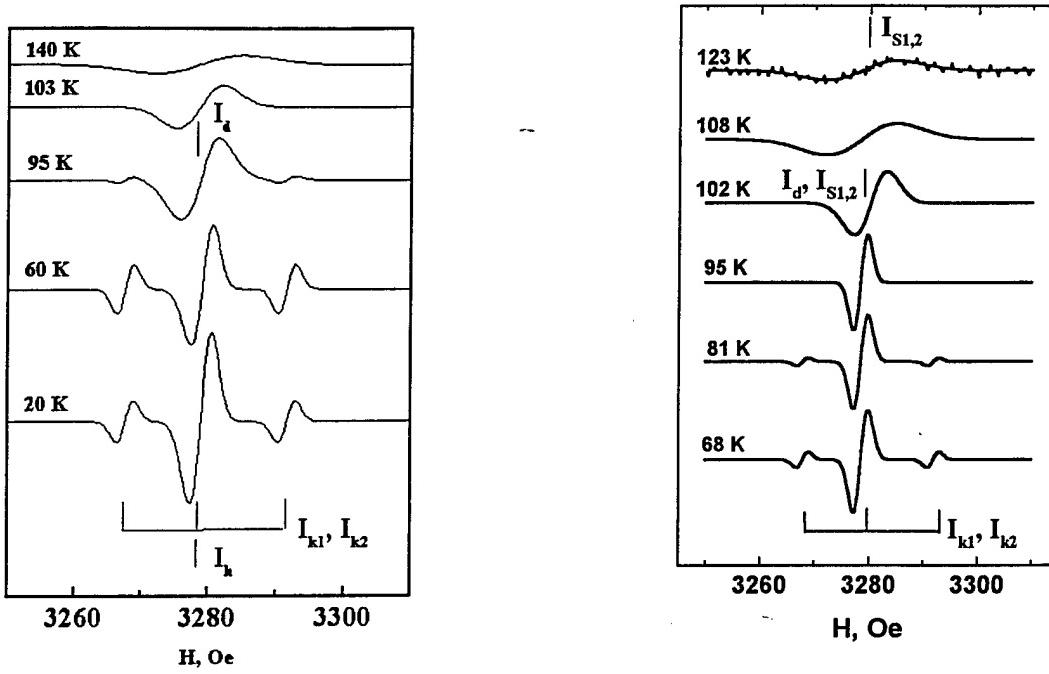
**a****b**

Fig.1. The thermal evolution of donor ESR spectrum in the bulk 6H SiC samples with donor concentration of ($N_D - N_A$): $2 \cdot 10^{18} \text{ cm}^3$ - a; $3 \cdot 10^{18} \text{ cm}^3$ - b.
 $\nu = 9.2 \text{ GHz}$. $H \perp c$.

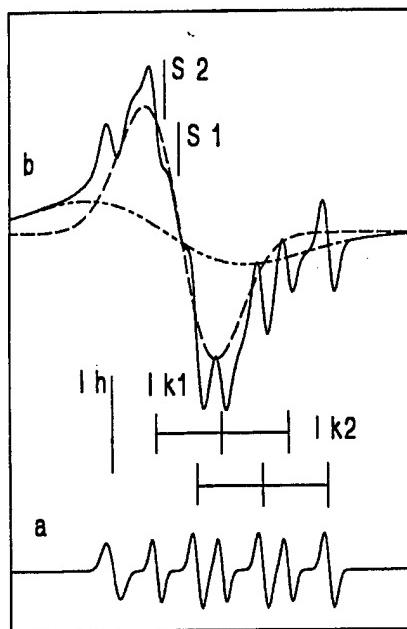


Fig.2. ESR spectrum of donors in bulk 6H SiC with ($N_D - N_A$): $2 \cdot 10^{18} \text{ cm}^3$ - a;
 $3 \cdot 10^{18} \text{ cm}^3$ - b. $\nu = 140 \text{ GHz}$, $T = 4.2 \text{ K}$. $H \parallel c$.

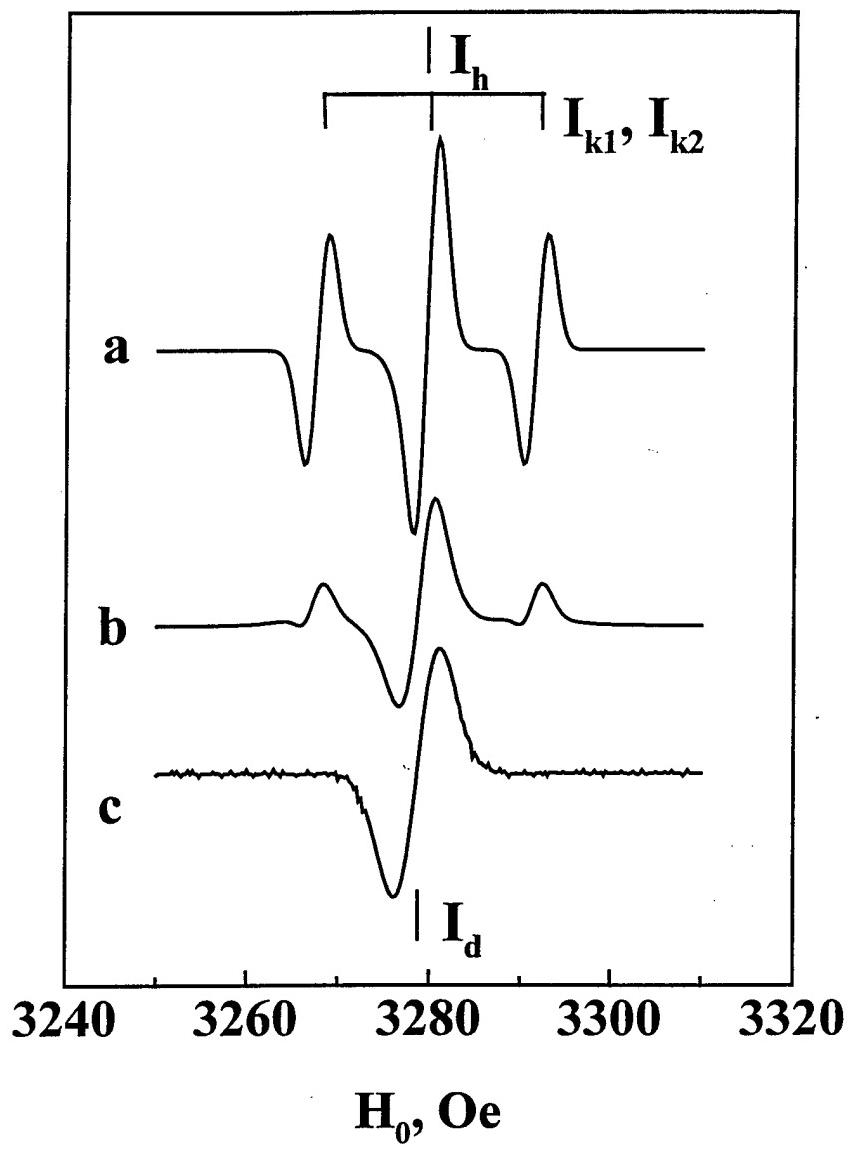


Fig.3. ESR spectrum of donors in 6H SiC at three level of microwave power:
 $P_a < P_b < P_c$. $(N_D - N_A) \approx 3 \cdot 10^{17} \text{ cm}^{-3}$. $\nu = 9 \text{ GHz}$, $T = 4.2 \text{ K}$.

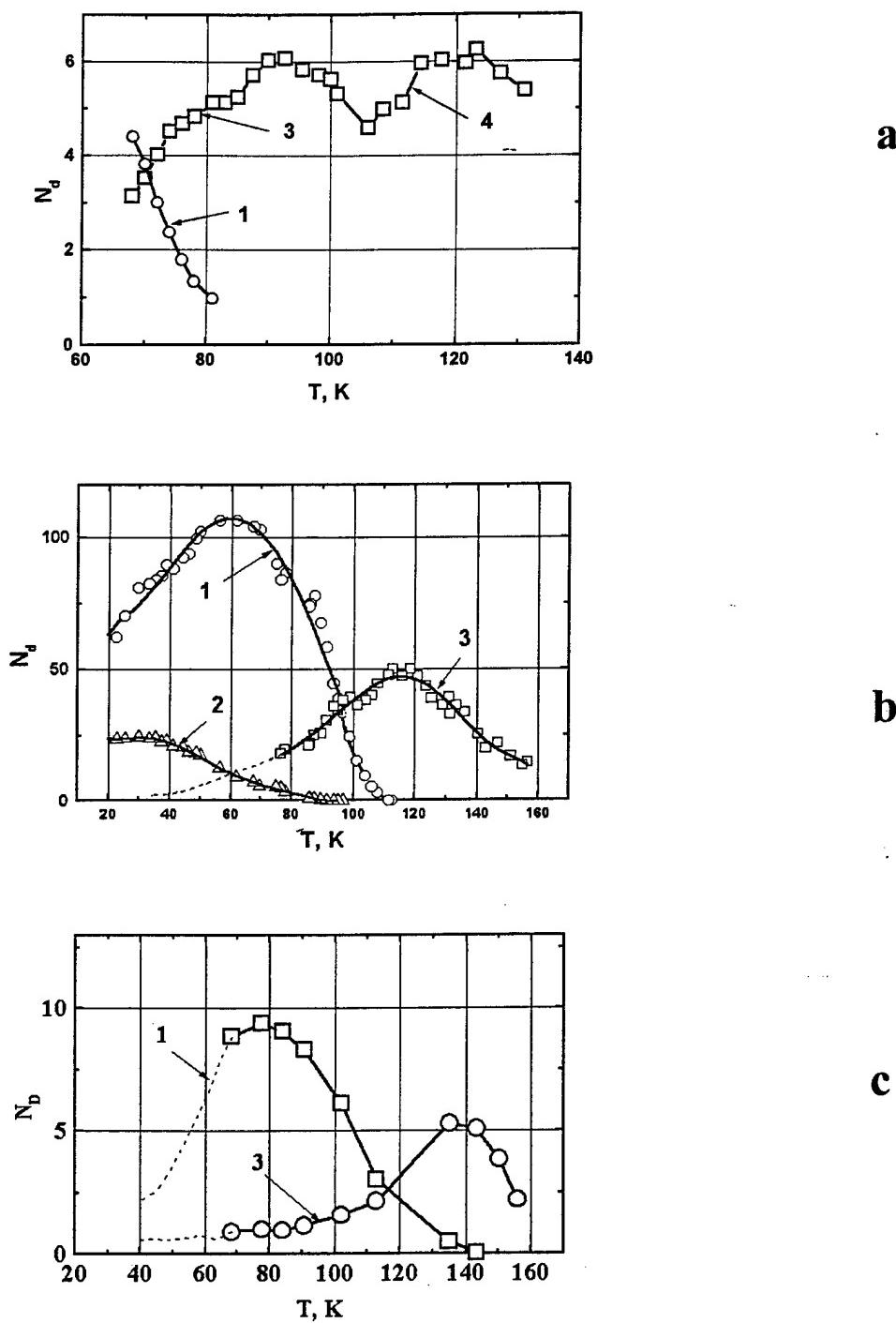


Fig.4. Temperature dependencies of the relative integral line intensities of donor ESR spectra in bulk 6H SiC with uncompensated donor concentration ($N_D - N_A$): $3 \cdot 10^{18} \text{ cm}^{-3}$ - a; $2 \cdot 10^{18} \text{ cm}^{-3}$ - b; $8 \cdot 10^{17} \text{ cm}^{-3}$ - c:
 1 - I_{k1}, I_{k2} ; 2 - I_h ; 3 - I_d , 4 - I_s .

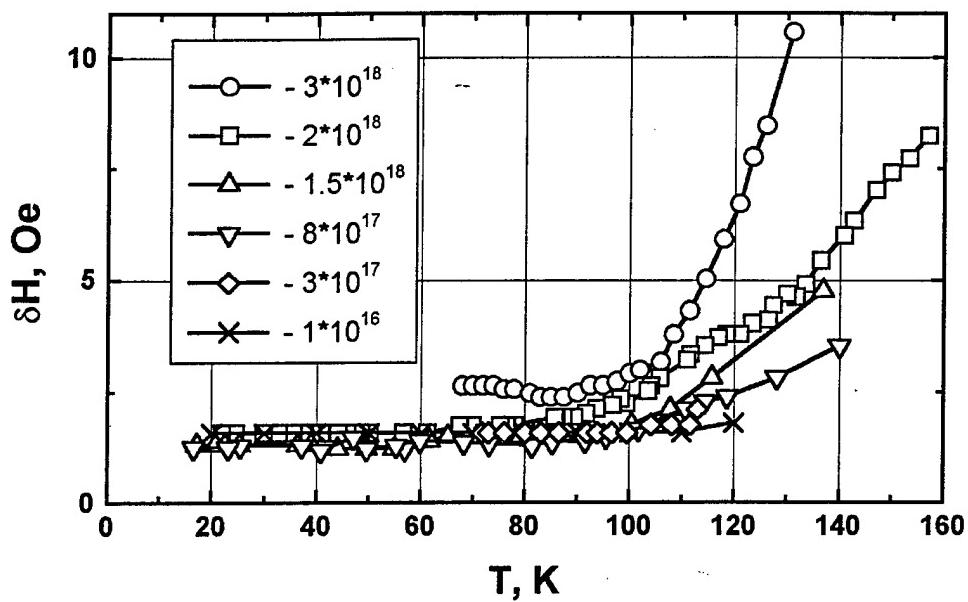


Fig. 5. Temperature dependence of the central triplet line width in 6H SiC for various donor concentration of ($N_D - N_A$). $h\nu = 9.2$ GHz.

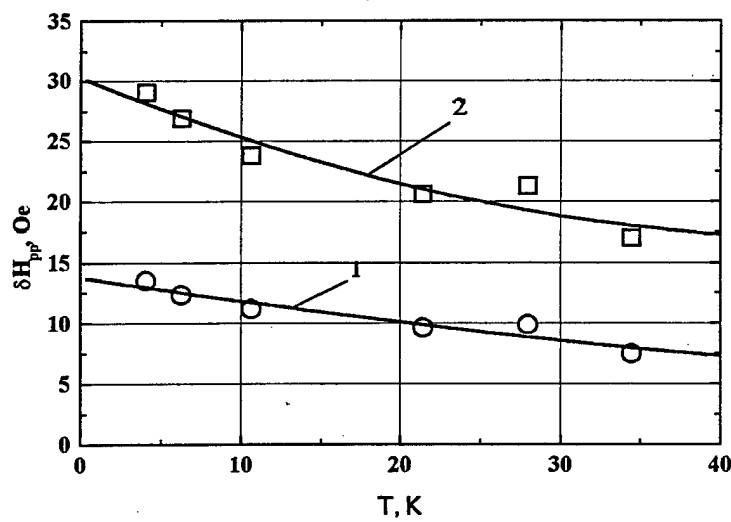


Fig.6.Temperature dependence of exchange I_{s1} (1) and I_{s2} (2)- line width in 6H SiC. $(N_D - N_A) \approx 3 \cdot 10^{18} \text{ cm}^{-3}$. $h\nu= 140$ GHz.

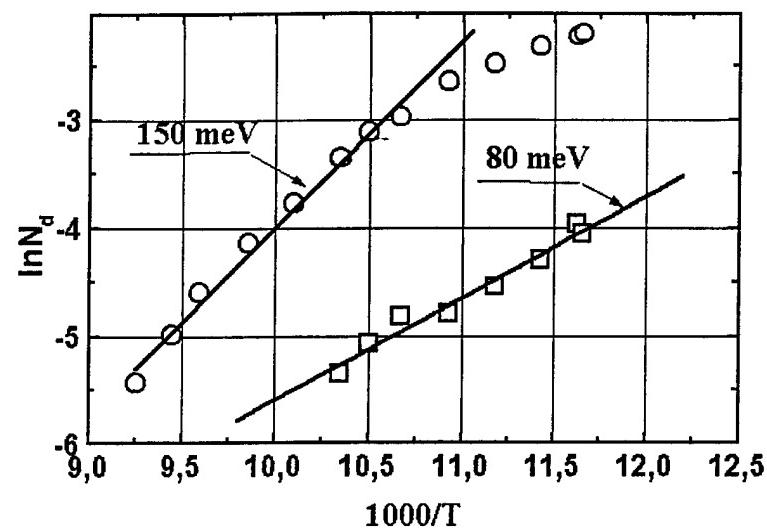
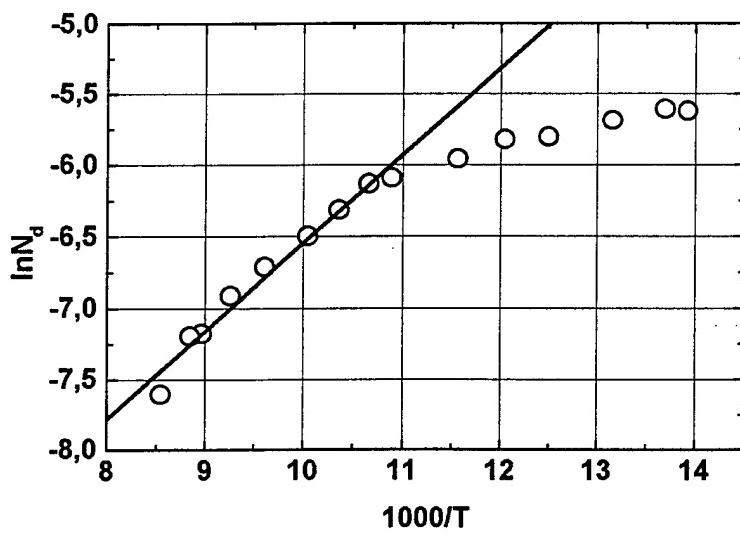
**a****b**

Fig.7. High temperature slope of the integral ESR line intensities of nitrogen on cubic and hexagonal sites in bulk 6H SiC with $(N_D - N_A) \approx 2 \cdot 10^{18} \text{ cm}^{-3}$. The solid lines are fitted by $\exp(-E_D/kT)$, where $E_D = 150 \text{ meV}$ for cubic sites and 80 meV for hexagonal site.

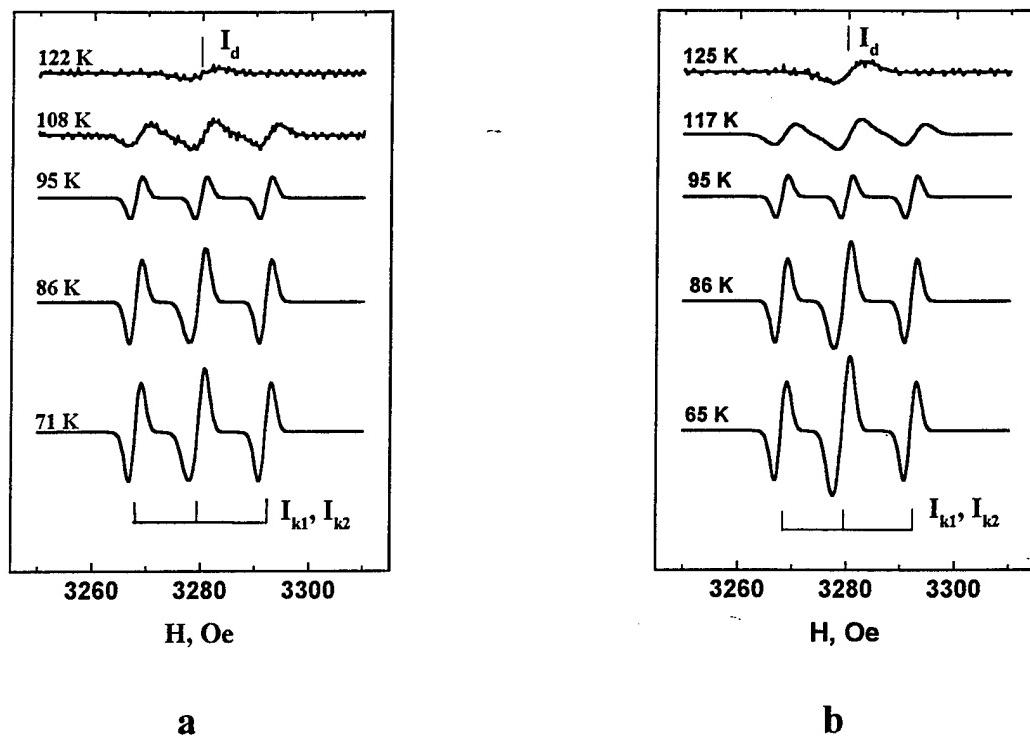


Fig.8. The thermal evolution of donor ESR spectrum in 6H SiC ($V_g = 0.5$ mm/h) with donor concentration of $(N_D - N_A)$: $(2 - 4) \cdot 10^{16} \text{ cm}^{-3}$ (sample I 90) - a; $(6 - 8) \cdot 10^{16} \text{ cm}^{-3}$ (sample I91.1) - b. $\nu = 9.2$ GHz, $H \perp c$.

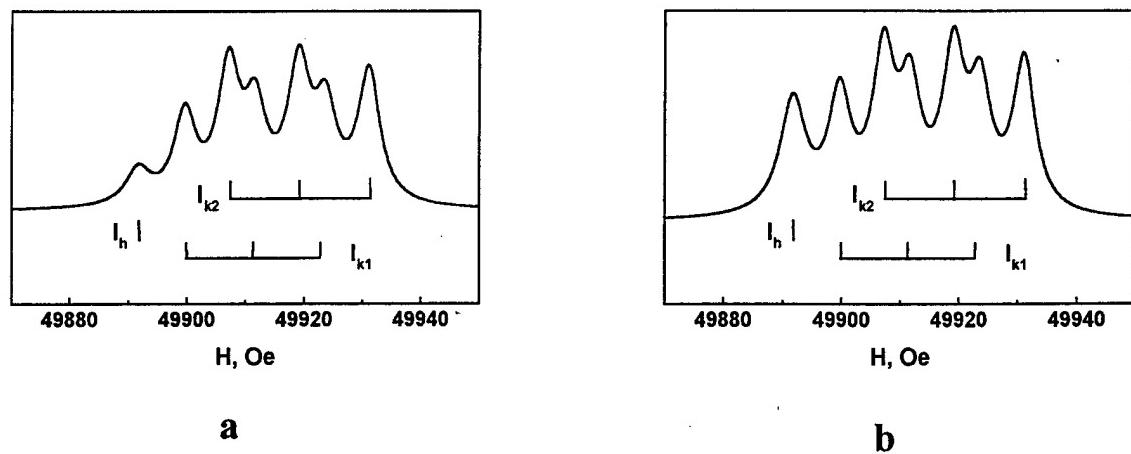


Fig.9. ESR spectrum of donors in 6H SiC ($V_g = 0.5$ mm/h) with $(N_D - N_A)$: $(2 - 4) \cdot 10^{16} \text{ cm}^{-3}$ (I90) - a; $(6 - 8) \cdot 10^{16} \text{ cm}^{-3}$ (I91.1) - b. $\nu = 140$ GHz, $T = 4.2\text{K}$, $H \parallel c$.

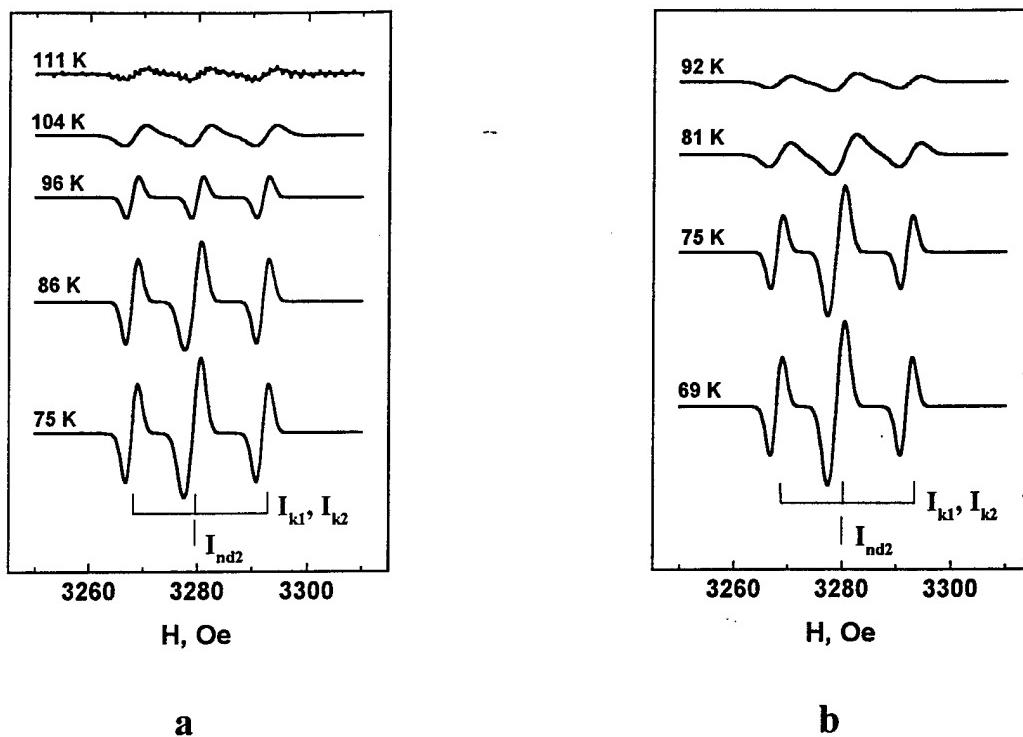


Fig. 10. The thermal evolution of donor ESR spectrum in 6H SiC ($V_g = 1.0 \text{ mm/h}$) with donor concentration of $(N_D - N_A)$: $(7 - 9) \cdot 10^{16} \text{ cm}^{-3}$ - a; $3 \cdot 10^{17} \text{ cm}^{-3}$ - b.
 $\nu = 9.2 \text{ GHz}, H \perp c$.

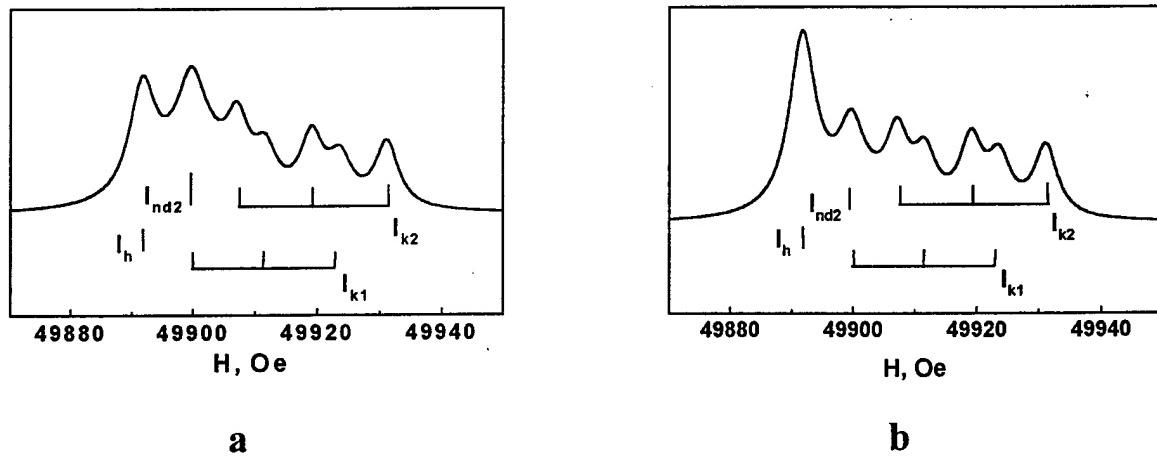


Fig. 11. ESR spectrum of donors in 6H SiC ($V_g = 1.0 \text{ mm/h}$) with $(N_D - N_A)$: $(7 - 9) \cdot 10^{16} \text{ cm}^{-3}$ - a; $3 \cdot 10^{17} \text{ cm}^{-3}$ - b. $\nu = 140 \text{ GHz}, T = 4.2 \text{ K}, H \parallel c$.

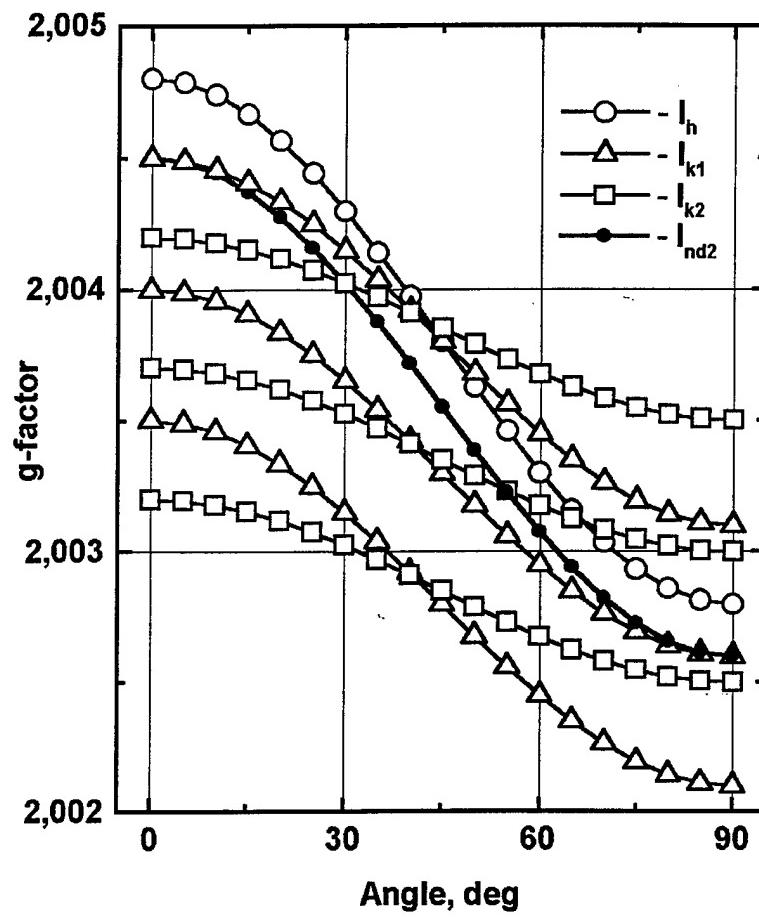


Fig. 12. ESR spectrum of donors in 6H SiC ($V_g = 1.0$ mm/h) with $(N_D - N_A)$:
 $(7 - 9) \cdot 10^{16} \text{ cm}^{-3}$. $\nu = 140$ GHz, $T = 4.2\text{K}$.

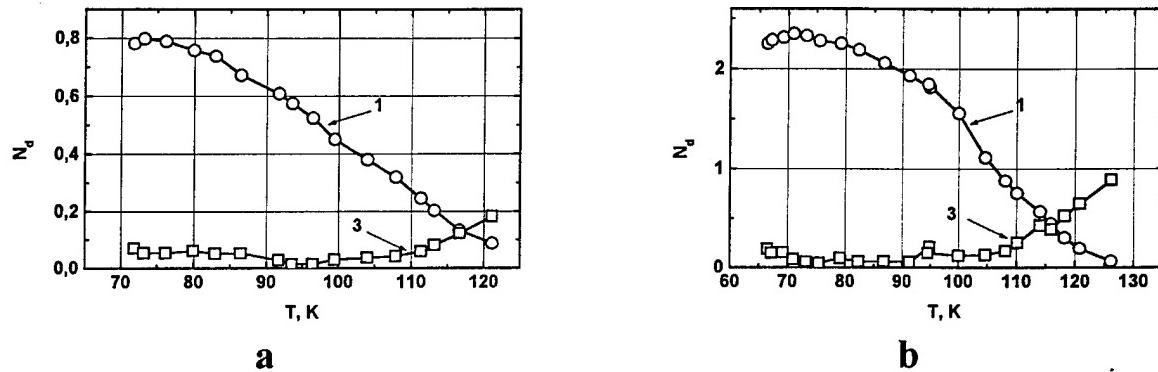


Fig.13. Temperature dependencies of the relative integral line intensities of donor ESR spectra in 6H SiC ($V_g = 0.5$ mm/h) with $(N_D - N_A)$: $(2 - 4) \cdot 10^{16} \text{cm}^{-3}$ (sample I 90) - a; $(6 - 8) \cdot 10^{16} \text{cm}^{-3}$ (sample I91.1) - b . 1 - I_{k1} , I_{k2} ; 3 - I_d .

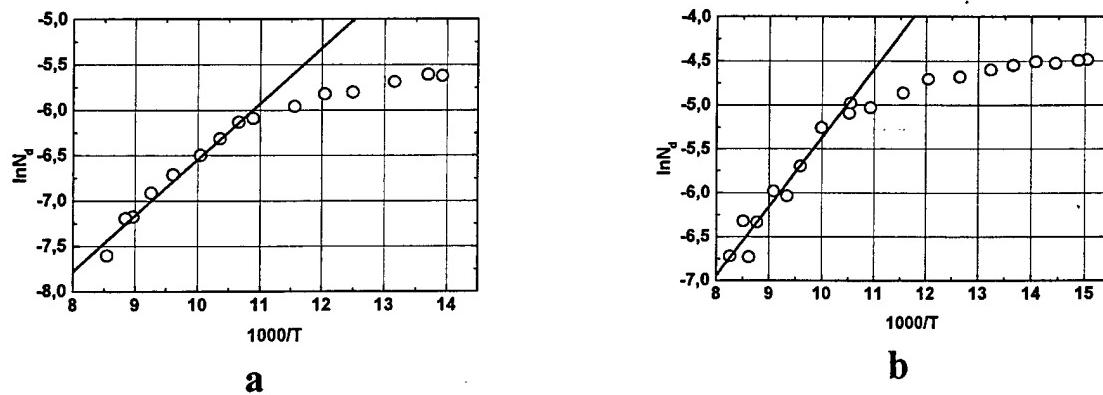


Fig.14. High temperature slope of the integral ESR line intensities of nitrogen on cubic sites in 6H SiC ($V_g = 0.5$ mm/h) with $(N_D - N_A)$: $(2 - 4) \cdot 10^{16} \text{cm}^{-3}$ (I 90) -a; $(6 - 8) \cdot 10^{16} \text{cm}^{-3}$ (I91.1) - b . The solid line is fitted by $\exp(-E_D/kT)$, where $E_D \approx 63$ meV.

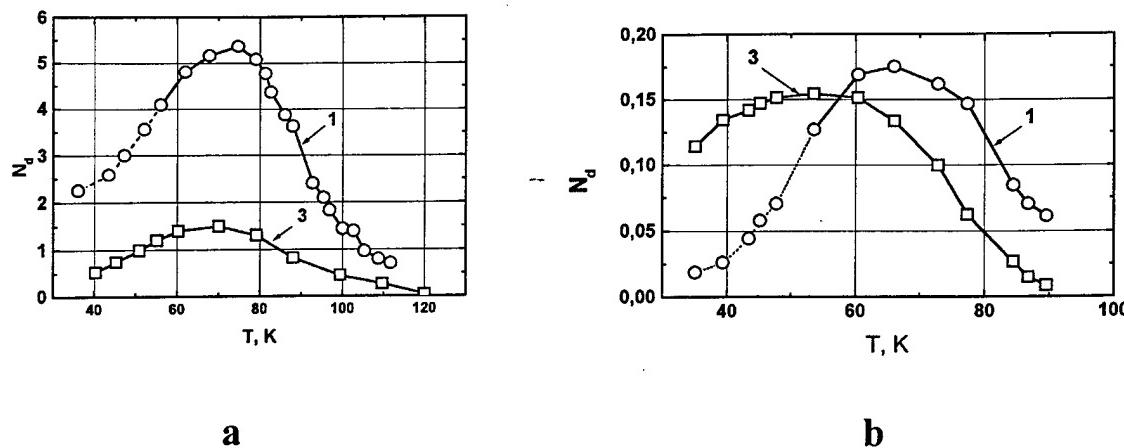


Fig.15. Temperature dependencies of the relative integral line intensities of donor ESR spectra in 6H SiC ($V_g = 1.0 \text{ mm/h}$) with $(N_D - N_A)$: $(7 - 9) \cdot 10^{16} \text{ cm}^3$ - a; $3 \cdot 10^{17} \text{ cm}^3$ - b . 1 - I_{k1} , I_{k2} ; 3 - I_{nd2}

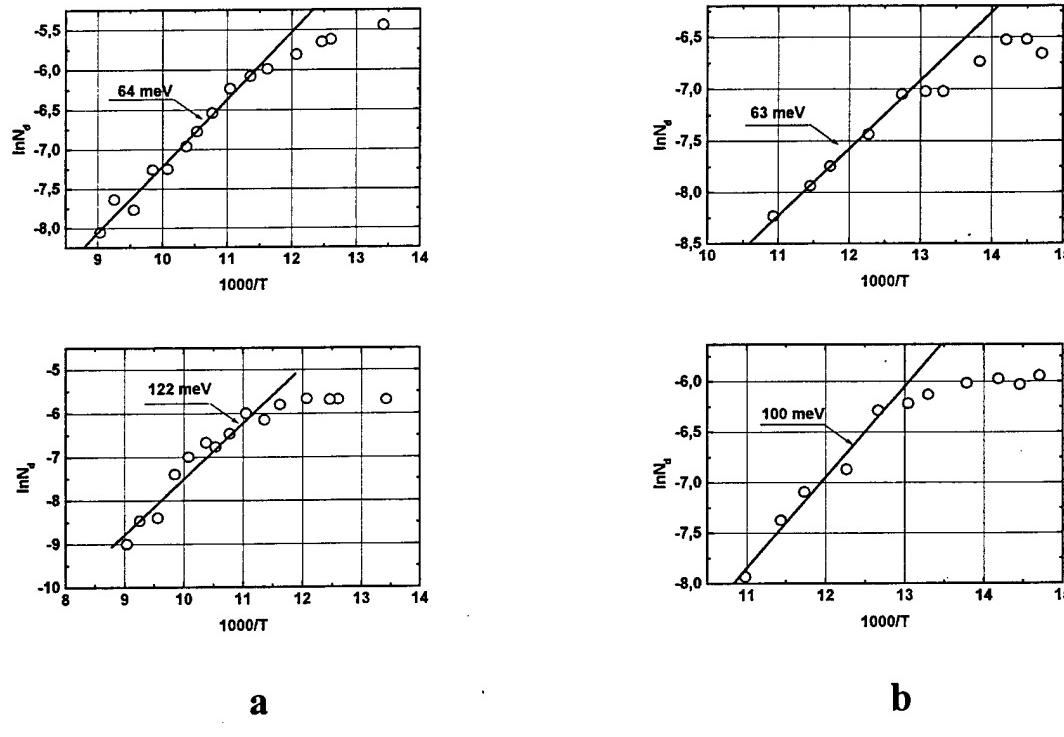


Fig.16. High temperature slope of the integral ESR line intensities of nitrogen on cubic sites and native defect I_{nd2} in 6H SiC ($V_g = 1.0 \text{ mm/h}$) with $(N_D - N_A)$: $(7 - 9) \cdot 10^{16} \text{ cm}^3$ - a; $3 \cdot 10^{17} \text{ cm}^3$ - b . The solid line is fitted by $\exp(-E_D/kT)$, where $E_D \approx 63 \text{ meV}$ for nitrogen on cubic sites and for native defect $E_D \approx 122 \text{ meV}$ (a), $E_D \approx 100 \text{ meV}$ (b).